

**37<sup>th</sup>**



**International Chemistry Olympiad**

**8 theoretical problems  
2 practical problems**

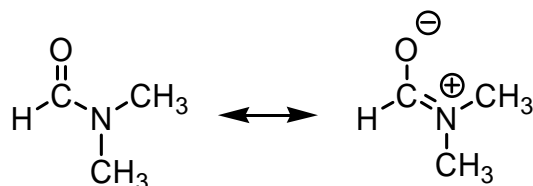
# THE THIRTY-SEVENTH INTERNATIONAL CHEMISTRY OLYMPIAD 16–25 JULY 2005, TAIPEI, TAIWAN

## THEORETICAL PROBLEMS

### PROBLEM 1

#### Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms N,N-dimethylformamide (DMF), which can be described as the following resonance structures.



1.1 Predict the order of melting points among N,N-dimethylformamide (compound **A**), N-methylacetamide ( $\text{CH}_3\text{CONHCH}_3$ , compound **B**), and propionamide (compound **C**,  $\text{CH}_3\text{CH}_2\text{CONH}_2$ ). Express your answer from high to low melting point as follows:

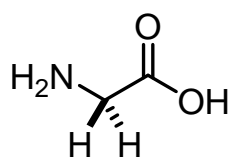
\_\_\_\_ > \_\_\_\_ > \_\_\_\_ (Insert compound codes **A**, **B**, **C**)

1.2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at  $1715\text{ cm}^{-1}$  for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.

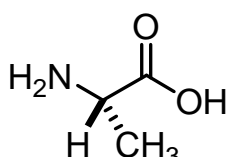
- (a)  $1660\text{ cm}^{-1}$  because of the shorter carbonyl bond length.
- (b)  $1660\text{ cm}^{-1}$  because of the longer carbonyl bond length.
- (c)  $1740\text{ cm}^{-1}$  because of the shorter carbonyl bond length.
- (d)  $1740\text{ cm}^{-1}$  because of the longer carbonyl bond length.

**1.3** Glycine ( $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ ) is an  $\alpha$ -amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

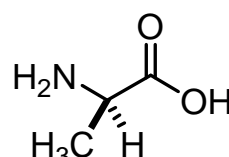
**1.4** When an  $\alpha$ -amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



D-Alanine (D-Ala)

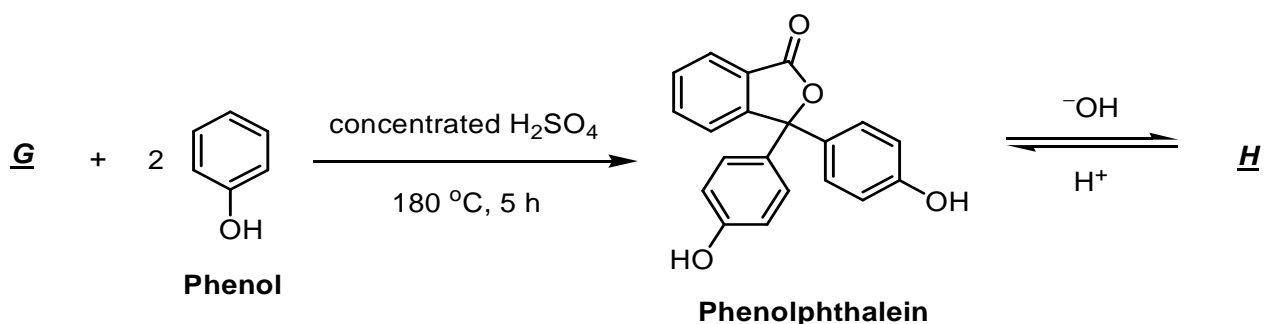
**1.5** Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

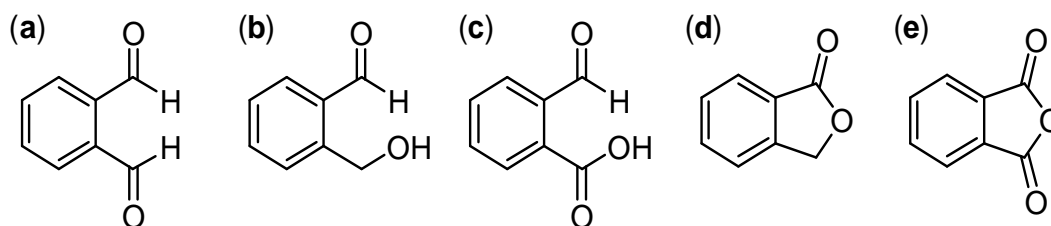
**1.6** Predict the binding affinity of phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) with a polyamide gel. Express your answer from high to low binding affinity as follows:

\_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_. (Insert compound codes **D**, **E**, and **F**)

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary colour. For example, phenolphthalein is a commonly used acid-base indicator, which is colourless in acidic and neutral solutions, but reddish pink in basic solutions ( $\text{pH}$  8.3 – 10.0).



- 1.7 Draw the structural formula of **H** derived from phenolphthalein that is attributable to the reddish pink colour in aqueous NaOH solution.
- 1.8 A simple way to prepare phenolphthalein is via condensation of compound **G** with 2 equivalents of phenol. What is the most effective reagent for **G** to accomplish this transformation? Select your answer from the following compounds.



## SOLUTION

- 1.1 The order of the melting points is: **C > B > A**

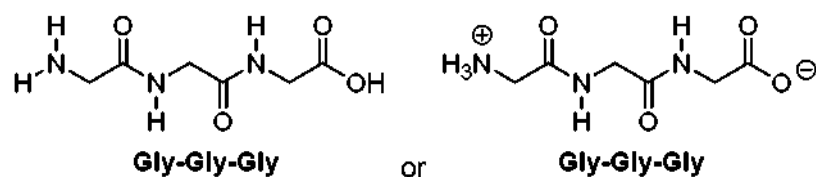
The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bonding, but not tertiary amide.

Propionamide, m.p. = 79 °C; *N*-methylacetamide, m.p. = 28 °C;

*N,N*-dimethylformamide, m.p. = -61 °C.

- 1.2 Correct: (b), 1660 cm<sup>-1</sup> due to a longer carbonyl bond length.

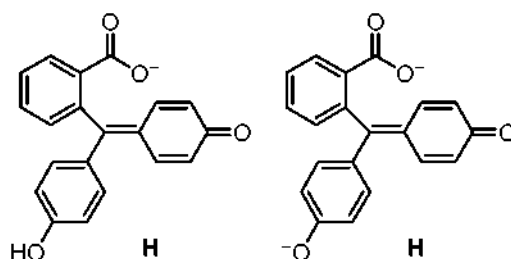
1.3



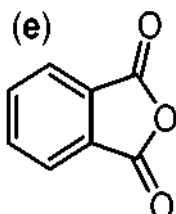
1.4 There are 27 possible tripeptides.

1.5 Among them, 26 tripeptides are optically active.Optically inactive tripeptide: H<sub>2</sub>N-GGG-OHOptically active tripeptides: H<sub>2</sub>N-GG<sup>L</sup>A-OH, H<sub>2</sub>N-GG<sup>D</sup>A-OH, H<sub>2</sub>N-G<sup>L</sup>AG-OH, H<sub>2</sub>N-<sup>L</sup>AG<sup>D</sup>A-OH, H<sub>2</sub>N-<sup>L</sup>A<sup>L</sup>A<sup>D</sup>A-OH, and so on.1.6 The relative binding strength with polyamide gel for phenol (compound **D**), 4-methylphenol (compound **E**) and 4-nitrophenol (compound **F**) is: **F > D > E**

1.7

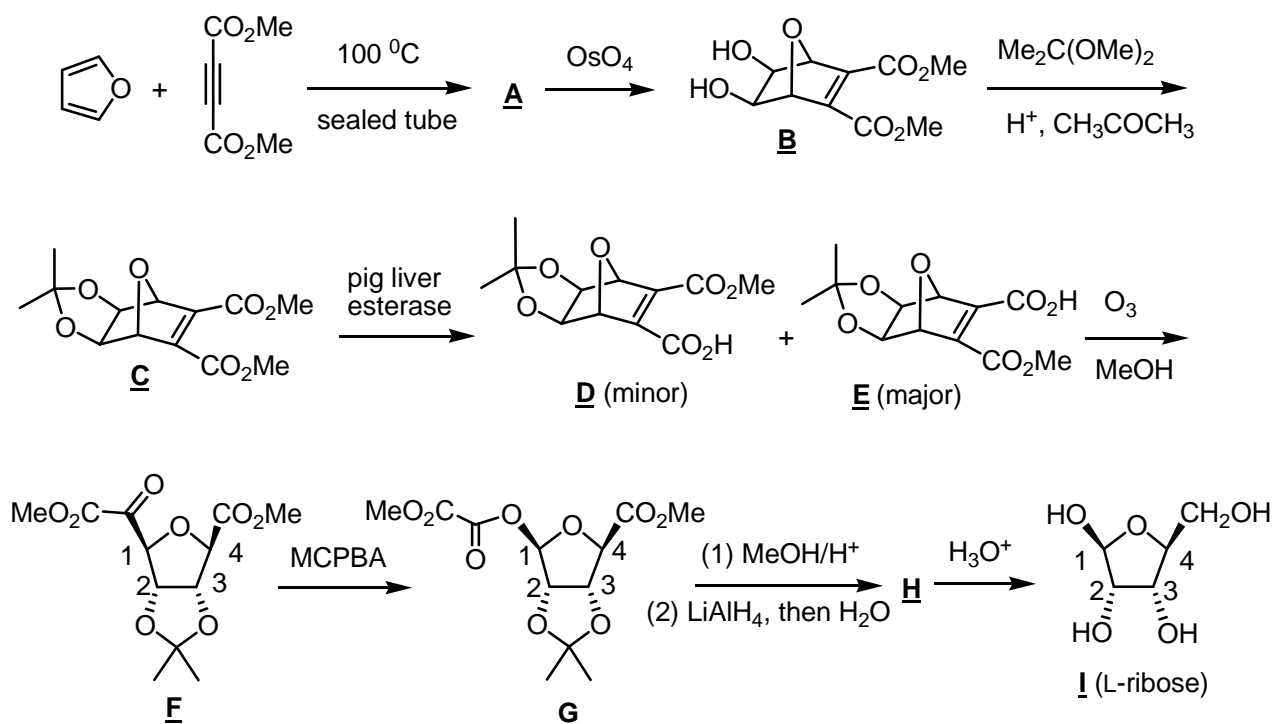
The range *pH* 8.3 – 10.0 for colour change of phenolphthalein.

1.8



**PROBLEM 2****Organic Synthesis and Stereochemistry**

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound **I**).



**2.1** Compound **A** has the molecular formula of  $C_{10}H_{10}O_5$ . Draw the structural formula of **A**.

**2.2** Given the chemistry described for reaction sequence **A** to **C**, indicate whether the following statements are true or false (Use T to represent true and F to represent false).

- \_\_\_ (a)  $OsO_4$  is an oxidizing agent in the reaction of **A** to **B**.
- \_\_\_ (b) MeOH is generated as a by-product in the reaction of **B** to **C**.
- \_\_\_ (c) Protons act as the catalyst in the transformation of **B** to **C**.
- \_\_\_ (d) **C** will still be formed albeit in lower yields in the absence of  $Me_2C(OMe)_2$ .

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was  $[\alpha]_D^{20} = -37.1^\circ$ . Further purification by recrystallization gave pure **E** with the optical rotation  $[\alpha]_D^{20} = -49.0^\circ$ .

**2.3** What is the molar ratio of **D/E** in the product mixture before the recrystallization?

Show your work.

**2.4** Reaction of **F** with meta-chloroperbenzoic acid (MCPBA) afforded **G** as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

\_\_\_\_\_ (a) The reaction was to oxidize compound **F**.

\_\_\_\_\_ (b) The oxygen atom inserted originated from MCPBA.

\_\_\_\_\_ (c) The *R/S* notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is  $C_9H_{16}O_5$ . Proton NMR data of **H** are listed as follows:

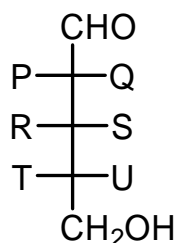
$^1H$  NMR ( $CDCl_3$ )  $\delta$  1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d,  $J = 6$  Hz, 1H), 4.74 (d,  $J = 6$  Hz, 1H), 4.89 (s, 1H).

**2.5** Draw the configurational formula of **H**.

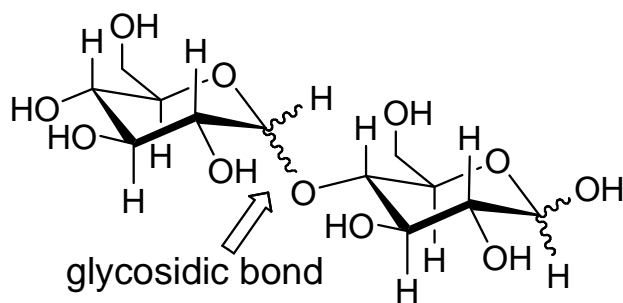
**2.6** Assign *R/S* notations for compound **I** at C-1, C-2, C-3 and C-4. Give your answers as follows:

C-1: \_\_\_\_\_; C-2: \_\_\_\_\_; C-3: \_\_\_\_\_; C-4: \_\_\_\_\_.

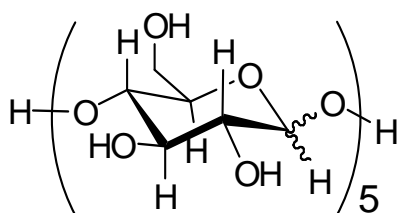
**2.7** What are the identities of P, Q, R, S, T and U in the Fischer projection of compound **I** (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



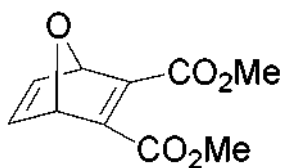
2.8 How many diastereoisomers would be obtained for pentasaccharide **J**, if it is derived from five units of D-glucose?



pentasaccharide **J** derived from D-glucose

## SOLUTION

2.1



2.2

T or F

- (a)  $\text{OsO}_4$  is an oxidizing agent in the reaction of **A** to **B**.
- (b)  $\text{MeOH}$  is generated as a by-product in the reaction of **B** to **C**.
- (c) Protons act as the catalyst in the transformation of **B** to **C**.
- (d) **C** will still be formed albeit in lower yields in the absence of  $\text{Me}_2\text{C}(\text{OMe})_2$

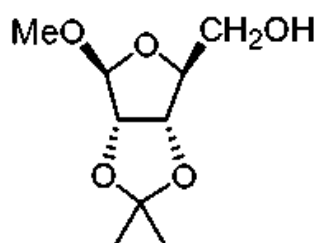


2.3 12.1 : 87.9 or 12.2 : 87.8

2.4 T or F

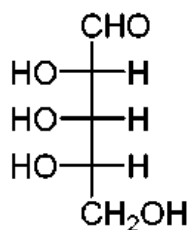
- I (a) The reaction was to oxidize compound **F**.  
I (b) The oxygen atom inserted originated from MCPBA.  
E (c) The *R/S* notation of C-1 remained unchanged before and after the reaction

2.5



2.6 C-1: S; C-2: S; C-3: R; C-4: S.

2.7



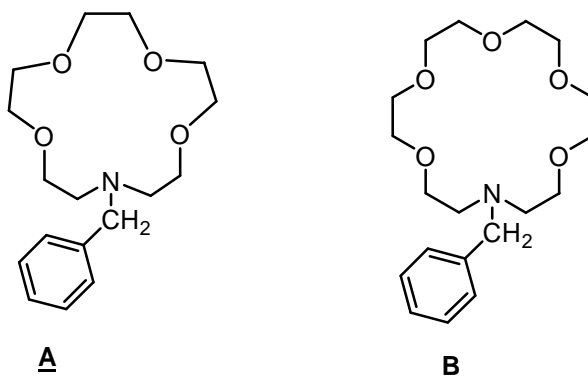
OH group for P, R, and T and H atom for Q, S, and U.

2.8 The number of stereoisomers =  $2^5$

**PROBLEM 3**

## Organic Photochemistry and Photophysics

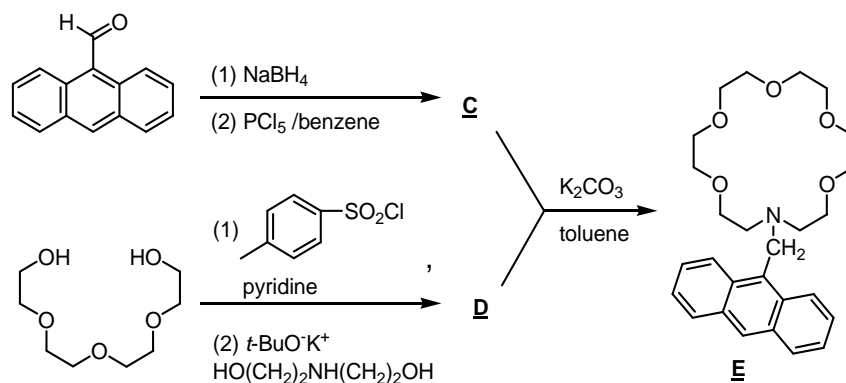
Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$ .



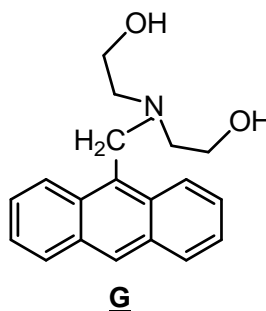
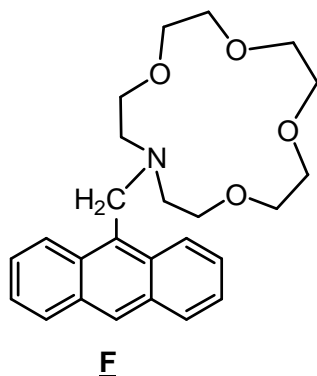
Metal ion	Radius (pm)	Binding constant ( $\log_{10} K$ )	
		Compound <b>A</b>	Compound <b>B</b>
$\text{Na}^+$	98	2.49	3.57
$\text{K}^+$	133	1.83	5.00
$\text{Cs}^+$	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

**3.1** Provide the structural formula of **C** and **D** in the following synthesis.

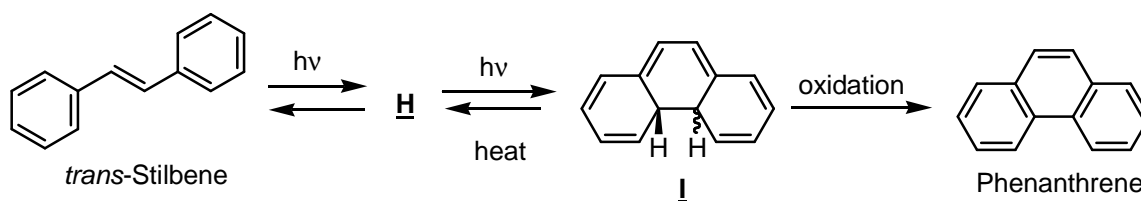


For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E**, **F**, and **G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



- 3.2** Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.
- (a) none of them      (b) **E** and **F** only      (c) **G** only      (d) all of them
- 3.3** By adding one equivalent of potassium acetate into a dilute solution ( $1 \times 10^{-5}$  M) of **E**, **F**, and **G** in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.
- (a) **E**      (b) **F**      (c) **G**
- 3.4** Upon adding one equivalent of metal acetate to a dilute solution of **F**, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.
- (a) sodium acetate   (b) potassium acetate   (c) cesium acetate   (d) doesn't make any difference

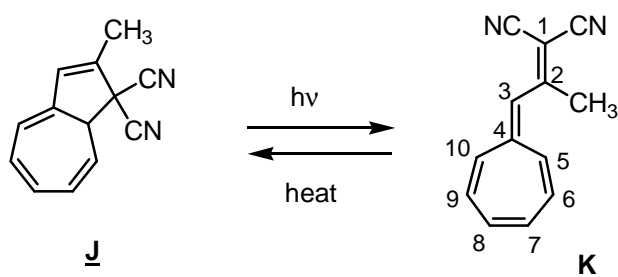
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of **I** gives phenanthrene.



3.5 Draw the structural formula of compound **H**?

3.6 What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound **I**?

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



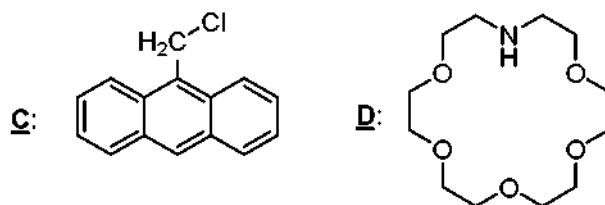
3.7 Which compound will absorb light with longer wavelength? Select your answer from the following choices: (a) **J** (b) **K**

3.8 Compound **K** can react with one equivalent of  $\text{CF}_3\text{CO}_2\text{H}$  to generate a stable aromatic salt. Which position of **K** is most likely protonated? Select your answer from the following choices.

- (a) C-2 (b) C-3 (c) C-4 (d) C-5

**SOLUTION**

3.1

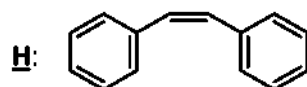


3.2 Correct is (d): All of them

3.3 Correct is (a): **E**

3.4 Correct is (a): sodium acetate

3.5



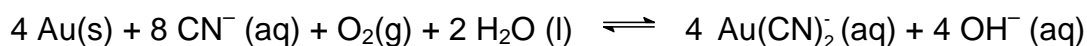
3.6 Trans

3.7 Correct is (b): **K**

3.8 Correct is (b): C-3

**PROBLEM 4****A**Gold Capital of Asia

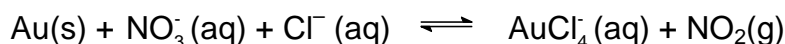
Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines in Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN<sup>-</sup>) solutions in the presence of air to form Au(CN)<sub>2</sub><sup>-</sup>, which is stable in aqueous solution.



**4.A-1** Draw a structure for Au(CN)<sub>2</sub><sup>-</sup> showing the spatial arrangements of the atoms.

**4.A-2** How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

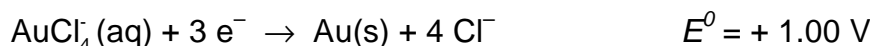
Aqua regia, a 3 : 1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:



**4.A-3** Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

**4.A-4** What are the oxidizing and reducing agents for 4.A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion AuCl<sub>4</sub><sup>-</sup> forms. Consider the following half-reactions:



An electrochemical cell can be formed from these two redox couples.

**4.A-5** Calculate the formation constant for AuCl<sub>4</sub><sup>-</sup> at 25 °C:

$$K = \frac{[\text{AuCl}_4^{-}]}{[\text{Au}^{3+}][\text{Cl}^{-}]^4}$$

**4.A-6** The function of HCl is to provide  $\text{Cl}^-$ . What is the purpose of the  $\text{Cl}^-$  for the above reaction. Select your answer from the following choices.

- (a)  $\text{Cl}^-$  is an oxidizing agent
  - (b)  $\text{Cl}^-$  is a reducing agent
  - (c)  $\text{Cl}^-$  is a complexing agent
  - (d)  $\text{Cl}^-$  is a catalyst
- 

## **B**

### Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of  $\text{HAuCl}_4$  is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of  $\text{NaBH}_4$ . Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

**4.B-1** Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

- (a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
- (b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

**4.B-2** The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry  $\text{AlCl}_4^-$  from an aqueous phase to an organic phase. Which

property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

- (a) one side of the molecule is electropositive, the other side is electronegative.
- (b) one side of the molecule is hydrophilic, the other side is hydrophobic.
- (c) one side of the molecule is acidic, the other side is basic.

**4.B-3** What is the function of  $\text{NaBH}_4$  in this preparation? Select your answer from the following choices.

- (a) reducing agent
- (b) oxidizing agent
- (c) neutralization agent
- (d) complexing agent

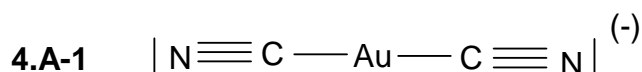
**4.B-4** If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

- (a)  $10^2$
- (b)  $10^3$
- (c)  $10^4$
- (d)  $10^5$

**4.B-5** What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

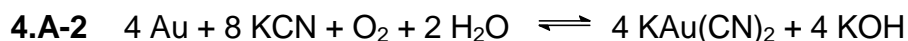
- (a) 20 – 30 %
- (b) 40 – 50 %
- (c) 60 – 70 %
- (d) 80 – 90 %

## SOLUTION



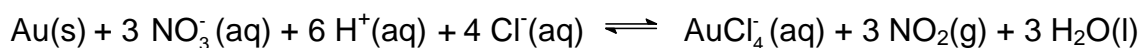
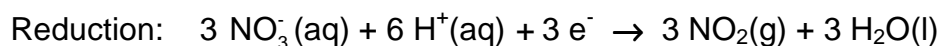
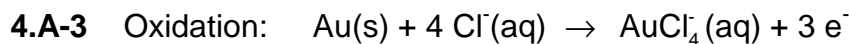
The structure of  $\text{Au}(\text{CN})_2^-$  is linear.





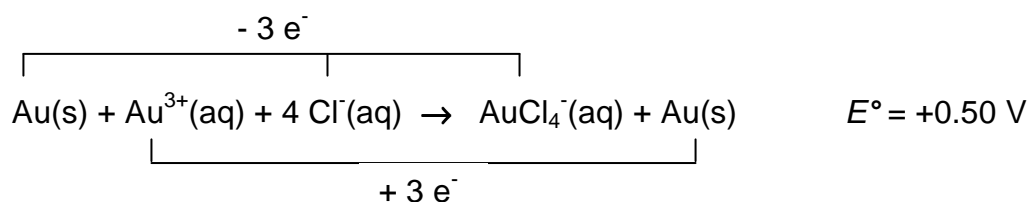
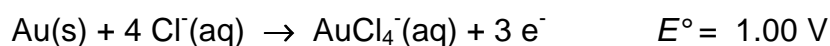
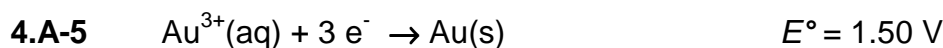
$$20 \text{ g} \div 197 \text{ g mol}^{-1} \approx 0.10 \text{ mol (Au)}$$

$$0.10 \text{ mol} \times (8/4) \times 65.12 \text{ g mol}^{-1} = 13.024 \text{ g KCN}$$



**4.A-4** Oxidizing agent:  $\text{HNO}_3$  or nitric acid

Reducing agent: Au



$$E = E^\circ - (0.059 / n) \log Q$$

At equilibrium,  $Q = K$ ,  $E = 0$ ,  $K = [\text{AuCl}_4^-] / [\text{Au}^{3+}] [\text{Cl}^-]^4$

$$E = (0.059 / n) \log K, \quad 0.50 = (0.059 / 3) \log K, \quad K = 10^{25.42} = 2.6 \times 10^{25}$$

$$\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$$

$$(-n F E_1^0) + (-n F E_2^0) = -RT \ln K$$

$$E^\circ = (RT / nF) \ln K = (0.059 / n) \log K,$$

$$0.50 = (0.059 / 3) \log K,$$

$$K = 10^{25.42} = 2.6 \times 10^{25}$$

4.A-6 Answer for multiple choice question: (c)

4.B-1 Answer for multiple choice question: (b)

4.B-2 Answer for multiple choice question: (b)

4.B-3 Answer for multiple choice question: (a)

4.B-4 Answer for multiple choice question: (b)

Calculation:

$$V_{\text{AuNPs}} = \frac{4}{3} \pi r_{\text{AuNPs}}^3$$

$$V_{\text{Au}} = \frac{4}{3} \pi r_{\text{Au}}^3$$

$$N_{\text{Au}} = \frac{V_{\text{AuNPs}}}{V_{\text{Au}}} = \frac{\frac{4}{3} \pi r_{\text{AuNPs}}^3}{\frac{4}{3} \pi r_{\text{Au}}^3} = \left( \frac{r_{\text{AuNPs}}}{r_{\text{Au}}} \right)^3 = \left( \frac{15 \text{ \AA}}{1,44 \text{ \AA}} \right)^3 \approx 1000$$

4B-5 Calculation:

Method 1:

$$4/3 \times \pi \times r_{\text{AuNPs}}^3 = 4/3 \times \pi \times r_{\text{Au}}^3 \times N_{\text{Au}}$$

$$r_{\text{AuNPs}}^3 = r_{\text{Au}}^3 \times N_{\text{Au}}$$

$$\text{Surface area of a gold nanoparticle: } S_{\text{AuNPs}} = 4 \pi r_{\text{AuNPs}}^2$$

$$S_{\text{AuNPs}} = 4 \pi r_{\text{Au}}^2 N_{\text{Au}}^{2/3}$$

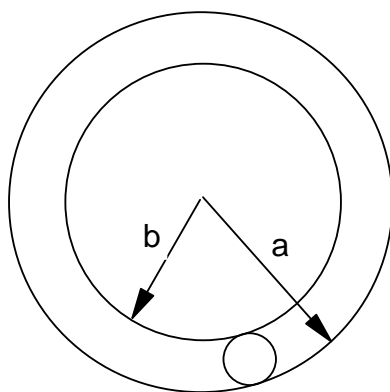
$$N_{\text{S}} \approx S_{\text{AuNPs}} / \pi r_{\text{Au}}^2 = 4 N_{\text{Au}}^{2/3}$$

$$P \approx N_{\text{S}} / N_{\text{Au}} = 4 / N_{\text{Au}}^{1/3}$$

$$N_{\text{Au}} \approx 1000$$

$$P \approx 40 \%$$

or Method 2:



$$a = r_{\text{AuNPs}}$$

$$b = r'_{\text{AuNPs}} = r_{\text{AuNPs}} - 2 r_{\text{Au}}$$

$$P \% = \frac{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}} - \frac{V'_{\text{AuNPs}}}{V_{\text{Au}}}}{\frac{V_{\text{AuNPs}}}{V_{\text{Au}}}} \times 100 \% = \frac{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3 - \left(\frac{r'_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3}{\left(\frac{r_{\text{AuNPs}}}{r_{\text{Au}}}\right)^3} \times 100 \% =$$

$$= \frac{(15 A)^3 - (12.12 A)^3}{(15 A)^3} \times 100 \% = 47 \%$$

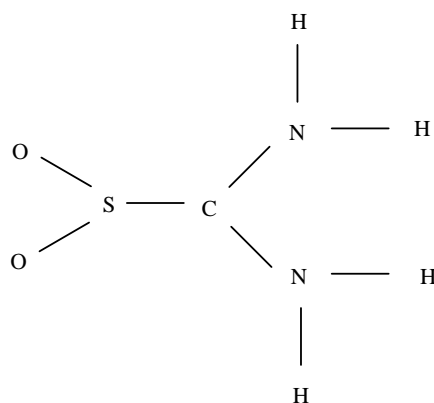
**PROBLEM 5****Lewis Structure**

5.1 Draw one Lewis structure for each of the following molecules.

- a) N<sub>2</sub>
- b) NH<sub>3</sub>
- c) O<sub>3</sub>
- d) SO<sub>3</sub>

5.2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, O<sub>2</sub>SC(NH<sub>2</sub>)<sub>2</sub>, has the following skeletal structure



5.3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5.4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5.3?

**5.4a** What is the geometry around the sulfur atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

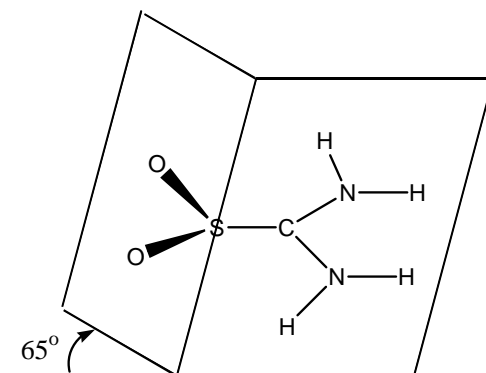
**5.4b** Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

**5.4c** Finally, what is the geometry around the N-atom? Select your answer from the following choices.

- a) trigonal pyramidal
- b) triangular planar
- c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



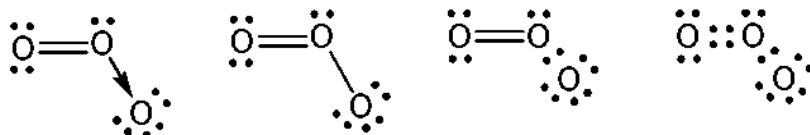
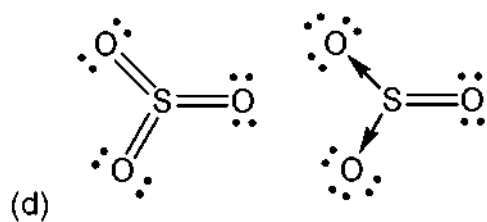
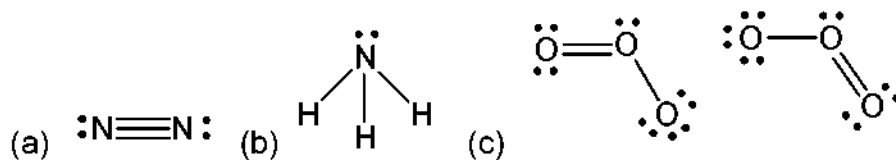
All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the SC(NH<sub>2</sub>)<sub>2</sub> plane is 65°.

**5.5** Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

\_\_\_\_\_

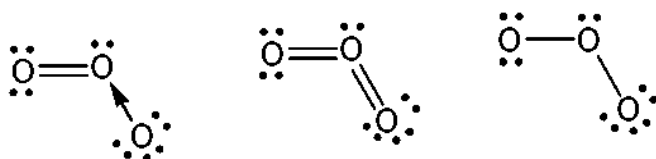
**SOLUTION**

5.1

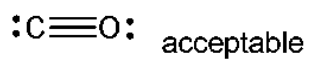
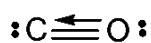


are all correct answers

But



are incorrect answers

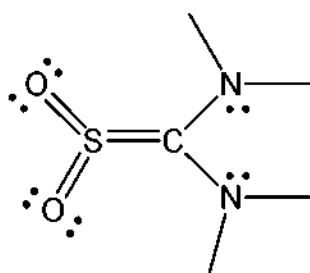


## 5.2

Formal charge  $C^{-1}$  ;  $O^{+1}$

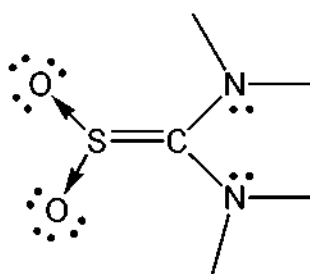
Oxidation state  $C^{2+}$  ;  $O^{2-}$

## 5.3



The structure

is correct.



The structure

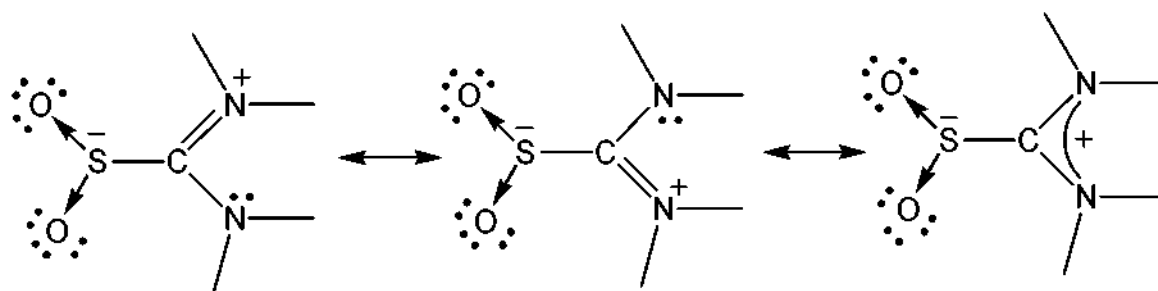
would have a formal charge and is incorrect.

5.4 Sulphur: (b) trigonal planar

Carbon: (b) trigonal planar

Nitrogen: (a) trigonal pyramidal

## 5.5

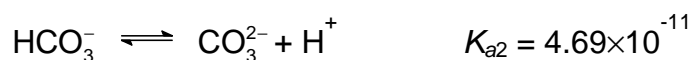
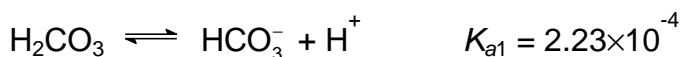
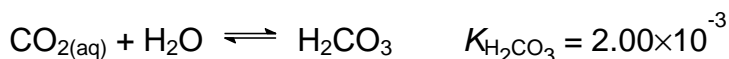
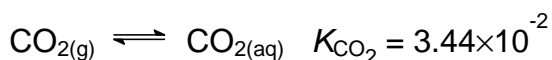


**PROBLEM 6****Alkalinity of Water and Solubility of CO<sub>2</sub>**

The capacity of water to accept H<sup>+</sup> ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and OH<sup>-</sup>. At *pH* values below 7, H<sup>+</sup> in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and OH<sup>-</sup> are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

The contributions made by different species to alkalinity depend upon *pH*. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:



Note: Calculations must be shown.

**6.1** Natural waters (river or lake water) generally contain dissolved CO<sub>2</sub>. The ratio of [H<sub>2</sub>CO<sub>3</sub>] : [HCO<sub>3</sub><sup>-</sup>] : [CO<sub>3</sub><sup>2-</sup>] in a water at [H<sup>+</sup>] = 1.00 × 10<sup>-7</sup> M will be:

(a) : 1.00 : (b). Calculate (a) and (b).

**6.2** Gaseous CO<sub>2</sub> in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of CO<sub>2(aq)</sub> (mol dm<sup>-3</sup>) in pure water that is in equilibrium with the unpolluted air at 1.01 × 10<sup>5</sup> Pa and 298 K containing 0.0360 % (molar ratio) CO<sub>2</sub>. (assuming standard pressure = 1.01 × 10<sup>5</sup> Pa).



If you are unable to solve this problem, assume that concentration of  $\text{CO}_2$  (aq) is equal to  $1.11 \times 10^{-5}$  M for further calculations.

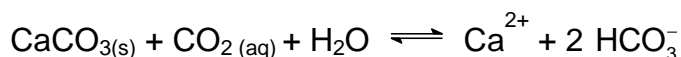
The solubility ( $S$ ) of  $\text{CO}_2$  in water can be defined as

$$S = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}].$$

The solubility of atmospheric  $\text{CO}_2$  in water that is in equilibrium with the unpolluted air at 298 K and  $1.01 \times 10^5$  Pa will vary with alkalinity.

- 6-3** Find the solubility of atmospheric  $\text{CO}_2$  in pure water ( $\text{mol dm}^{-3}$ ). Neglect dissociation of water.
- 6.4** Find the solubility of atmospheric  $\text{CO}_2$  ( $\text{mol dm}^{-3}$ ) in a  $1.00 \times 10^{-3}$   $\text{mol dm}^{-3}$  NaOH solution.

At 298 K,  $1.01 \times 10^5$  Pa unpolluted air is in equilibrium with natural water saturated with  $\text{CaCO}_3$ . The following main equilibrium may exist:



- 6.5** Calculate the equilibrium constant for the above equation.

If you are unable to solve this problem, assume that equilibrium constant  $K_{\text{eq}} = 5.00 \times 10^{-5}$  for further calculations.

- 6.6** Calculate the concentration of  $\text{Ca}^{2+}$  ( $\text{mg dm}^{-3}$ ) in  $\text{CaCO}_3$ -saturated natural water that is in equilibrium with atmospheric  $\text{CO}_2$ .

If you are unable to solve this problem, assume that concentration of  $\text{Ca}^{2+}_{(\text{aq})} = 40.1$   $\text{mg dm}^{-3}$  for further calculations.

- 6.7** Find the alkalinity ( $\text{mol/L}$ ) of the above solution.
- 6.8** In an underground lake saturated with  $\text{CaCO}_3$ , the water has a high content of  $\text{CO}_2$ . The concentration of  $\text{Ca}^{2+}$  in this lake was found to be as high as  $100 \text{ mg dm}^{-3}$ . Assume the lake and the air above is a closed system, calculate the effective pressure of  $\text{CO}_2$  (Pa) in air which is in equilibrium with this  $\text{Ca}^{2+}$  content.

**SOLUTION**

6.1  $[H^+] = 1.00 \times 10^{-7}$

$$K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23 \times 10^{-4},$$

$$[HCO_3^-] / [H_2CO_3] = 2.23 \times 10^3$$

$$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69 \times 10^{-11},$$

$$[CO_3^{2-}] / [HCO_3^-] = 4.69 \times 10^{-4}$$

$$[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = 4.48 \times 10^{-4} : 1.00 : 4.69 \times 10^{-4}$$

6.2  $p(\text{CO}_2(\text{aq})) = 1.01 \times 10^5 \text{ Pa} \times 3.60 \times 10^{-4} = 36.36 \text{ Pa}$

$$[\text{CO}_2(\text{aq})] = K_{\text{CO}_2} \times p(\text{CO}_2) = 0.0344 \times (36.36 \text{ Pa} / 1.01 \times 10^5 \text{ Pa}) = 1.24 \times 10^{-5}$$

(If you are unable to solve this problem, for further calculations assume that  $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$ .)

**6.3**

(a) Solubility =  $[\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-]$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.48 \times 10^{-8}$$

$$\text{and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) = K_{a2} = 4.69 \times 10^{-11}$$

both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

From 6-2:  $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$ ,

$$[H^+] = [HCO_3^-] = 2.35 \times 10^{-6}$$

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [HCO_3^-] = 1.24 \times 10^{-5} + 2.35 \times 10^{-6} = 1.48 \times 10^{-5} \text{ mol dm}^{-3}$$

(b) (Using  $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$  for calculation)

$$\text{Solubility} = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [HCO_3^-]$$

$$([\text{H}_2\text{CO}_3] = [\text{CO}_2(\text{aq})] \times K_{\text{H}_2\text{CO}_3} = 2.22 \times 10^{-8} \text{ and } [\text{CO}_3^{2-}] = K_{a2} / ([H^+] / [HCO_3^-]) =$$

$K_{a2} = 4.69 \times 10^{-11}$  both can be neglected.)

$$[H^+][HCO_3^-] / [\text{CO}_2(\text{aq})] = K_{a1} K_{\text{H}_2\text{CO}_3} = (2.23 \times 10^{-4}) (2.00 \times 10^{-3}) = 4.46 \times 10^{-7}$$

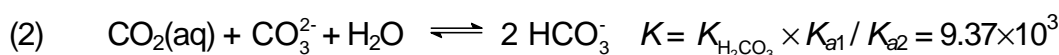
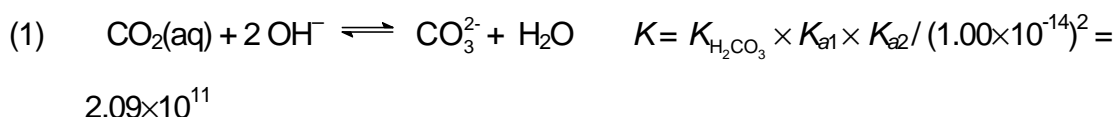
From 6.2:  $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{H}^+] = [\text{HCO}_3^-] = 2.225 \times 10^{-6}$

Solubility =  $[\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] = 1.11 \times 10^{-5} + 2.225 \times 10^{-6} = 1.34 \times 10^{-5}$

**6.4** (Using  $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$  for calculation)

In  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$  NaOH solution the solubility of  $\text{CO}_2$  will be much higher because of the following reactions:



Combining (1) and (2):  $\text{CO}_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad K = 4.43 \times 10^7$

With such a large  $K$  value all  $\text{OH}^-$  will finally be converted to  $\text{HCO}_3^-$ .

$$[\text{HCO}_3^-] = 1.00 \times 10^{-3}$$

$$[\text{OH}^-] = 1.82 \times 10^{-6}$$

$$[\text{H}^+] = 5.49 \times 10^{-9} \quad [\text{CO}_3^{2-}] = 8.54 \times 10^{-6}$$

$$\begin{aligned} \text{Solubility} &= [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \approx [\text{CO}_2(\text{aq})] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = \\ &= 1.24 \times 10^{-5} + 1.00 \times 10^{-3} + 8.54 \times 10^{-6} = 1.02 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \mathbf{6.5} \quad K_{\text{eq}} &= K_{\text{sp}} \times K_{\text{H}_2\text{CO}_3} \times K_{\text{a1}} / K_{\text{a2}} = (4.50 \times 10^{-9}) \times (2.00 \times 10^{-3}) \times (2.23 \times 10^{-4}) / (4.69 \times 10^{-11}) = \\ &= 4.28 \times 10^{-5} \end{aligned}$$

(If you are unable to solve this problem, assume that  $K_{\text{eq}} = 5.00 \times 10^{-5}$  for further calculations.)

**6.6**

(a) (Using  $K_{\text{eq}} = 4.28 \times 10^{-5}$  and  $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$  for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**:  $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-] / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**:  $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$

$[\text{Ca}^{2+}] = 0.510 \times 10^{-3} = 20.5 \text{ mg dm}^{-3}$

- (b) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**:  $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**:  $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5177 \times 10^{-3} = 20.75 \text{ mg dm}^{-3}$

- (c) (Using
- $K_{\text{eq}} = 5.00 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$
- for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**:  $K = 5.00 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**:  $[\text{CO}_2(\text{aq})] = 1.24 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.5372 \times 10^{-3} = 21.53 \text{ mg dm}^{-3}$

- (d) (Using
- $K_{\text{eq}} = 4.28 \times 10^{-5}$
- and
- $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$
- for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

From **6.5**:  $K = 4.28 \times 10^{-5} = [\text{Ca}^{2+}][\text{HCO}_3^-]^2 / [\text{CO}_2(\text{aq})] = [\text{Ca}^{2+}] (2 [\text{Ca}^{2+}])^2 / [\text{CO}_2(\text{aq})]$

From **6.2**:  $[\text{CO}_2(\text{aq})] = 1.11 \times 10^{-5}$

$[\text{Ca}^{2+}] =$

$0.4916 \times 10^{-3} = 19.70 \text{ mg dm}^{-3}$

(If you are unable to solve this problem, assume that  $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$  for further calculations.)

**6.7**  $\text{HCO}_3^-$  is the major species in solution.

The  $pH$  of the solution can be estimated as  $pH = (pK_{a1} + pK_{a2})/2 = (3.65 + 10.33) / 2 = 6.99 \approx 7.00$ ,

where  $K_{a1}$  and  $K_{a2}$  are the dissociation constants of  $\text{H}_2\text{CO}_3$ .

At  $pH$  7.00, both  $[\text{OH}^-]$  and  $[\text{H}^+]$  can be neglected. Besides,  $[\text{CO}_3^{2-}] \ll [\text{HCO}_3^-]$

(from **6.1**)

Alkalinity =  $[\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \approx [\text{HCO}_3^-]$

From 6-6, mass balance,  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

- (a)  $1.02 \times 10^{-3}$  (using  $[\text{Ca}^{2+}]_{(\text{aq})}$  from 6.6 (a))
- (b)  $1.035 \times 10^{-3}$  (using  $[\text{Ca}^{2+}]_{(\text{aq})}$  from 6.6 (b))
- (c)  $1.0744 \times 10^{-3}$  (using  $[\text{Ca}^{2+}]_{(\text{aq})}$  from 6-6 (c))
- (d)  $0.9831 \times 10^{-3}$  (using  $[\text{Ca}^{2+}]_{(\text{aq})}$  from 6-6 (d))
- (e)  $2.00 \times 10^{-3}$  (assuming  $[\text{Ca}^{2+}]_{(\text{aq})} = 40.1$ )

Alkalinity = (a) or (b) or (c) or (d) or (e)

### 6.8

- (a) (Using  $K_{\text{eq}} = 4.28 \times 10^{-5}$  for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Inserting into } K_{\text{eq}} = 4.28 \times 10^{-5} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2(\text{aq})]} = 4 \frac{[\text{Ca}^{2+}]}{[\text{CO}_2(\text{aq})]}$$

$$[\text{CO}_2(\text{aq})] = 1.46 \times 10^{-3}$$

$$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 4.28 \times 10^3 \text{ Pa}$$

- (b) (Using  $K_{\text{eq}} = 5.00 \times 10^{-5}$  for calculation)

Mass balance :  $[\text{HCO}_3^-] = 2 [\text{Ca}^{2+}]$

$$[\text{Ca}^{2+}] = 100 \text{ mg dm}^{-3} = 2.50 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Inserting into } K_{\text{eq}} = 5.00 \times 10^{-5} = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2(\text{aq})]} = 4 \frac{[\text{Ca}^{2+}]}{[\text{CO}_2(\text{aq})]}$$

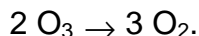
$$[\text{CO}_2(\text{aq})] = 1.25 \times 10^{-3}$$

$$p_{\text{CO}_2} = ([\text{CO}_2(\text{aq})] / K_{\text{CO}_2}) \times 1.01 \times 10^5 \text{ Pa} = 3.67 \times 10^3 \text{ Pa}$$

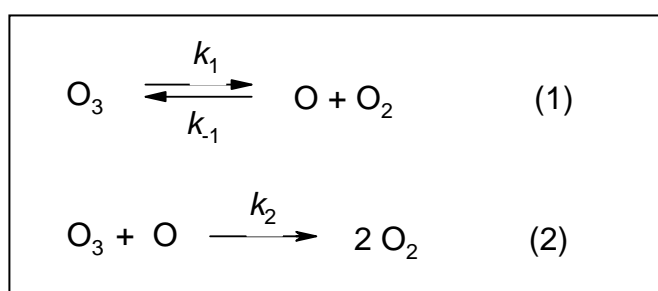
**PROBLEM 7****Kinetic Behaviour of Ozone**

Ozone ( $O_3$ ) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.

For the overall reaction of ozone decomposition,



One of the proposed mechanisms is expressed as



where  $k_1$ ,  $k_{-1}$ , and  $k_2$  are the rate constants.

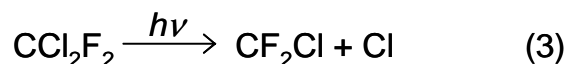
**7.1** According to the above mechanism what are the differential rate equations for the formation (or consumption) of  $O_3$ ,  $O_2$ , and  $O$  at time  $t$ , assuming step 2 is irreversible.

**7.2** Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of  $O$  atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the  $O_3$  depletion as a function of  $O_2$  and  $O_3$  concentrations.

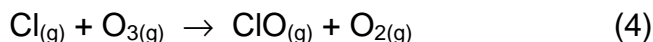
**7.3** Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is  $d[O]/dt = 0$ , show that the rate equation is:

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ( $2O_3 \rightarrow 3O_2$ ) in the upper atmosphere is catalyzed by Freons. For instance, when  $CCl_2F_2$  (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of  $CCl_2F_2$  may give rise to  $Cl$  atoms according to the following reaction:



7.4 Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:



Assuming a two-step mechanism, propose the second step in the mechanism.

7.5 The activation energy for Cl-catalyzed destruction of ozone is  $2.1 \text{ kJ mol}^{-1}$ , while the activation energy for the reaction without the presence of catalyst is  $14.0 \text{ kJ mol}^{-1}$ . Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at  $25^\circ\text{C}$ . Assume the frequency factor is the same for each reaction.

## SOLUTION

$$\begin{aligned} 7.1 \quad -\frac{d[\text{O}_3]}{dt} &= k_1 [\text{O}_3] - k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}_2]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] - 2k_2 [\text{O}_3][\text{O}] \\ -\frac{d[\text{O}]}{dt} &= -k_1 [\text{O}_3] + k_{-1} [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] \end{aligned}$$

7.2 Equilibrium constant  $K$  is expressed as

$$K = \frac{[\text{O}][\text{O}_2]}{[\text{O}_3]} = \frac{k_1}{k_{-1}}$$

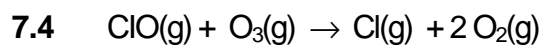
$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]}$$

$$-\frac{d[\text{O}_3]}{dt} = k_2[\text{O}_3][\text{O}] = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

$$7.3 \quad -\frac{d[\text{O}]}{dt} = 0$$

$$-k_1 [\text{O}_3] + k_1 [\text{O}][\text{O}_2] + k_2 [\text{O}_3][\text{O}] = 0$$

$$\text{Thus } -\frac{d[\text{O}_3]}{dt} = 2k_2 [\text{O}_3][\text{O}] = \frac{2k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$



**7.5** According to equation  $k = A \exp(-E_a/RT)$ ,  
the ratio of rate constants yields

$$\text{Ratio} = \exp[(14.0 - 2.1) \times 1000 / (8.314 \times 298)] = 122.$$

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## PROBLEM 8

### Protein Folding

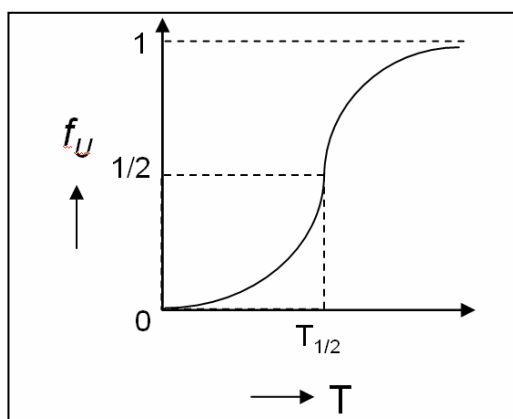
Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:



where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively.  $K(T)$  is the equilibrium constant for the process at absolute temperature  $T$ .

- 8.1** What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?
- 8.2** What is the standard free energy change of the process ( $\Delta G^\circ(T)$ ) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.
- 8.3** If  $(C_N)_{\text{eq}}$  and  $(C_U)_{\text{eq}}$  denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by  $f_U = (C_U)_{\text{eq}}/C$ . Deduce an expression for  $f_U$  in terms of the equilibrium constant  $K$ . Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by  $f_U = 1/2$  and  $T = T_{1/2}$ . The latter is often referred to as the denaturation temperature. At temperatures higher than  $T_{1/2}$ ,  $f_U$  increases above  $1/2$ , but at temperatures lower than  $T_{1/2}$ ,  $f_U$  decreases below  $1/2$ .

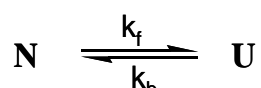
**8.4** What is the sign of  $\Delta G^\circ(T)$  at temperatures below and above  $T_{1/2}$ ? Select your answer from the following choices.

- Negative both below and above  $T_{1/2}$ .
- Positive both below and above  $T_{1/2}$ .
- Positive below  $T_{1/2}$ , but negative above  $T_{1/2}$ .
- Negative below  $T_{1/2}$ , but positive above  $T_{1/2}$ .

**8.5** How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above  $T_{1/2}$  and (ii) decreases below  $T_{1/2}$ ? Select your answer from the following choices.

- Decrease in both cases.
- Increase in both cases.
- Increases above  $T_{1/2}$ , but decreases below  $T_{1/2}$ .
- Decreases above  $T_{1/2}$ , but increases below  $T_{1/2}$ .

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:



where  $k_f$  and  $k_b$  denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

**8.6** For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant  $K$  and the rate constants  $k_f$  and  $k_b$ ?

**8.7** Derive a rate law for the overall process, that is  $dC_U/dt$  in terms of only rate constants,  $C_U$  and  $(C_U)_{eq}$ .

**SOLUTION**

8.1 Answer: 1

8.2 Answer: 0 kJ mol<sup>-1</sup>

$$8.3 \quad f_U = \frac{C_U^{\text{eq}}}{C_N^{\text{eq}} + C_U^{\text{eq}}} = \frac{\frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}}{1 + \frac{C_U^{\text{eq}}}{C_N^{\text{eq}}}} = \frac{K}{1 + K}$$

8.4 Correct answer is (c). Positive below  $T_{1/2}$ , but negative above  $T_{1/2}$ 8.5 Correct answer is (d). Decreases above  $T_{1/2}$ , but increases below  $T_{1/2}$ .8.6 Answer:  $K = k_f / k_b$ 

$$8.7 \quad \begin{aligned} dC_U/dt &= k_f C_N - k_b C_U \\ &= k_f (C - C_U) - k_b C_U = k_f C - k_f C_U - k_b C_U = k_f C - (k_f + k_b) C_U \end{aligned} \quad (1)$$

$$K = k_f / k_b = (C_U)_{\text{eq}} / (C_N)_{\text{eq}}$$

$$1 / K = k_b / k_f = (C_N)_{\text{eq}} / (C_U)_{\text{eq}}$$

$$\Rightarrow k_b / k_f + 1 = (C_N)_{\text{eq}} / (C_U)_{\text{eq}} + 1$$

$$\Rightarrow (k_b + k_f) / k_f = [(C_N)_{\text{eq}} + (C_U)_{\text{eq}}] / (C_U)_{\text{eq}}$$

$$\Rightarrow (k_b + k_f) / k_f = C / (C_U)_{\text{eq}}$$

$$C = [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \quad (2)$$

Now substitute  $C$  obtained from eq (2) to eq (1).

$$\text{We get } k_f \{ [(k_b + k_f) (C_U)_{\text{eq}}] / k_f \} - (k_f + k_b) C_U$$

$$\Rightarrow [(k_b + k_f) (C_U)_{\text{eq}}] - (k_f + k_b) C_U$$

$$\Rightarrow - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

So we get

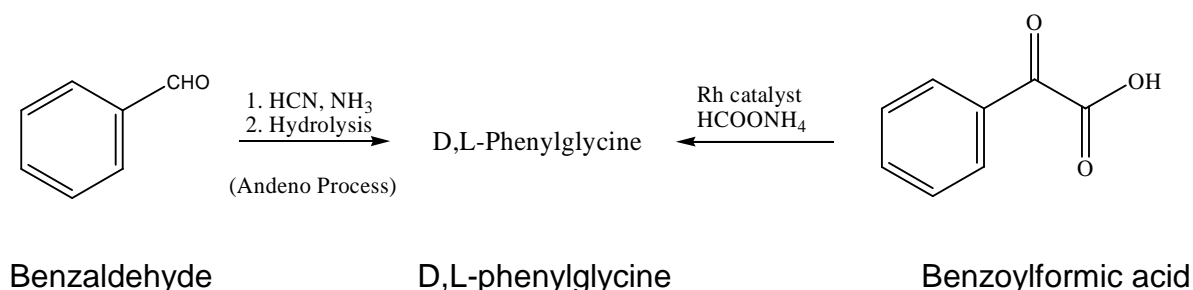
$$dC_U/dt = - (k_f + k_b) [C_U - (C_U)_{\text{eq}}]$$

## PRACTICAL PROBLEMS

### PROBLEM 1 (Practical)

#### The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of  $\beta$ -lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH<sub>3</sub> following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as *R*- and *S*-isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H<sub>2</sub>O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H<sub>2</sub>O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

#### EXPERIMENTAL PROCEDURE

##### Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

- To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass

on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (NOTE: irritant, do not contact with skin), 7.57 g of ammonium formate ( $\text{HCO}_2\text{NH}_4$ ), 37.2 mg of Rh catalyst (NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!) and  $22 \text{ cm}^3$  of the pre-mixed solvents at ambient temperature.

- Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (NOTE: the solvent is air cooled, so there is no tap water running through the condenser.) The temperature of the water bath needs to be maintained in the range of 68 to 72 °C by adjusting the thermostat of the hot plate/stirrer.
- The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.
- Add  $15 \text{ cm}^3$  of deionized water to the resulting mixture and stir for 10 minutes.
- Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol ( $10 \text{ cm}^3$  each). For each washing, **break the aspirator pressure**, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.
- For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 °C for 1.5 hour.

During the drying period you can start working on Experiment 2 (analytical experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

- Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by  $^1\text{H}$  NMR spectrum

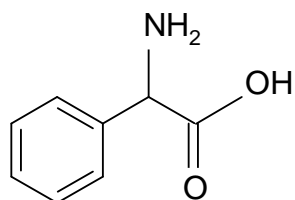
analysis. Turn in the product in a vial (**blue label** with  $^1\text{H}$  NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

## **Step 2. Enantiomeric Resolution of D,L-phenylglycine by (+)-Camphorsulfonic Acid [(+)-CSA]**

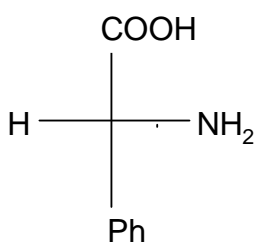
1. To a 25 cm<sup>3</sup> round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 cm<sup>3</sup>) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 °C. Keep the mixture at this temperature for 10 minutes until it turns clear.
2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.
3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 cm<sup>3</sup> each).
4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 °C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).
5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (pink label labelled with  $[\alpha]_D$  and your student code) and give the sample vial to the lab assistant. The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

**SOLUTION**

1.4 Structural formula (A) and stereochemical formula (B) of the isolated phenylglycine:  
(Task appeared in the answer sheet only.)



A



B

**PROBLEM 2 (Practical)****Identification of Unknown Inorganic Samples**

## Note

- (1) This practical exercise is a kind of "spot test". You can do it on the pallet or on a sheet of black film (for white precipitate).
- (2) Please check all items written in the equipment and reagent list.
- (3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.
- (4) The volume of each unknown solution is about  $1.5 \text{ cm}^3$  (about 30 drops). No more reagents or samples will be provided.
- (5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.
- (6) Make sure the switch on the battery box is closed.
- (7) You will get 8 points for each correct identification.

## Introduction

There are 12 unknown samples in your plastic bag: 9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the List of Unknown Inorganic Samples carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about  $1.5 \text{ cm}^3$  solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M ( $\text{mol dm}^{-3}$ ).

The unknown samples are as follows:

HCl	$\text{H}_2\text{O}_2$	$\text{H}_2\text{SO}_4$	$\text{ZnCl}_2$	$\text{NH}_4\text{SCN}$
NaOH	$\text{Na}_2\text{CO}_3$	$\text{Na}_2\text{SO}_3$	$\text{BaCl}_2$	$\text{K}_4\text{Fe}(\text{CN})$

6

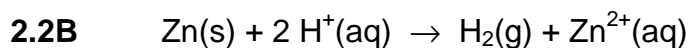
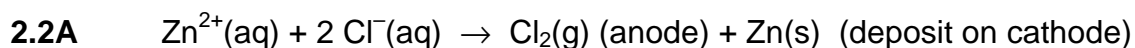
## Note

- 1) Two unknown samples are duplicates.



- 2) The crystal water (. H<sub>2</sub>O) is omitted in the formulas listed above.
- 2.1** Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.
- 2.2** In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.
- A. Write the electrolysis equation that would help you confirm that an unknown sample is ZnCl<sub>2</sub>.
- B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).
- 

## **SOLUTION**



or

